FINAL TECHNICAL REPORT

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PROJECT SUMMARY

This research program was generally concerned with the application of Ballistic Electron Emission Microscopy (BEEM) and related scanning tunneling microscopy (STM) techniques to the study of interfacial ballistic transport in a range of electronic materials, and with the extension of BEEM to locally examine aspects, consequences, and possible applications of elastic and inelastic electronic scattering processes at both Schottky barrier interfaces and thin film overlayers. The overall program objectives were:

A. To advance the understanding of key aspects of ballistic electron transport phenomena and of its study by ballistic electron emission microscopy.

B. To apply BEEM to the microscopic study of the transport properties of electronic interfacial systems of current scientific interest and potential technological importance.

C. To explore and study novel, low energy, ~ 3 eV, hot electron interactions with thin film materials and interfacial systems so as to develop a more complete understanding of the microscopic nature of detrimental hot electron effects in electronic materials, and to establish the potential for nanolithographic applications of such effects.

To accomplish these objectives, we pursued experiment projects that:

1. Examined and directly demonstrated in several different ways the high spatial resolution of the BEEM technique.

2. Developed a new model for ballistic electron transport across non-epitaxial Schottky barrier interfaces that explains the insensitivity of such transport on the crystalline orientation of the semiconductor without an ad-hoc invocation of strong elastic scattering at the interface.

3. Developed and applied a new three terminal BEEM measurement configuration that has successfully tested and extended important aspects of the theoretical understanding of BEEM.

4. Extensively studied and quantified the effects of ion beam etching and implantation on ballistic transport in processed metal-semiconductor interfaces, and from these experiments established a more successful model of BEEM transport.

5. Further examined hot electron modification or subsurface ballistic electron lithography effects in various types of Au - Si Schottky barrier systems and established a qualitative description of this phenomena.

In the following, each of these efforts are summarized. More complete information can be found in the resulting technical publications which are listed at the end of this report.

1. BEEM Resolution Studies

For quite some time after the invention of BEEM there had been considerable controversy and uncertainty regarding the possible spatial resolution that could be obtained with this technique. There have been various arguments put that strong elastic scattering was impacting the ballistic electron transport in thin film Schottky barrier systems. In general these arguments were developed in large part to explain the lack of sensitivity of BEEM transport to the Si surface orientation in Au - Si diodes. In this model there is a large degree of elastic scattering as an injected beam of electrons moves through a thin metal film towards a buried Schottky barrier interface. Hence this scattering broadens the injected beam and thus greatly blurs the spatial resolution of a BEEM measurement. But there was no well accepted understanding of what the origin of this scattering might be. Initial experiments by the JPL group to examine this issue suggested that the elastic scattering was not strong, but the results were not sufficiently compelling to resolve the question. We successfully examined this basic issue with two separate approaches. In one case SiO_2 windows were microfabricated on a silicon surface, thereby creating very high resolution structures at the Au - Si interface that have very high BEEM contrast.

These provided the first reported BEEM images of *ex-situ* fabricated nanostructures and showed a resolution of better than one nanometer. In the other experiment the hot electron modification effect was employed to create very small, ~ 5 nm, features at passivated Au - Si interfaces. Such features were imaged with BEEM with better than 1 nm resolution. Both of these observations are in sharp contrast to what would be obtained in the presence of strong elastic scattering in the Au layer and vividly demonstrate the high resolution capabilities of BEEM.

2. Ballistic Transport Across Non-Epitaxial Interfaces

If strong elastic scattering is not present in ballistic transport through thin metal layers, then the question arises as to how one explains the lack of sensitivity of BEEM measurements to the surface orientation of the semiconductor. For example, electron propagation in the (111) direction of Si requires a substantial transverse momentum component for injected electron energies just above the Schottky barrier height. Yet BEEM spectra on Si(111) and Si(100) surfaces are essentially indistinguishable experimentally. Ludeke and Bauer have explained such observations by invoking in an ad-hoc manner, strong elastic scattering at the interface, but not in the bulk of the film. This assumption is consistent both with the high spatial resolution of BEEM measurements and with the observed interfacial transport properties. There has been however no direct verification of the presence of such interfacial scattering. We pursued a more fundamental explanation for this effect that took into account the quantum mechanical aspects of electronic transport in crystalline lattices. We successfully performed model calculations that showed that when an electron moves from the Au lattice into the Si lattice, the lack of a close match in the lattice periodicity results in a strong refraction of the incident electron wave. This provides the propagating wave with sufficient transverse momentum to quantitatively account for the observed high BEEM transmissivity across an interface for which simple momentum conservation arguments would predict a very low transmissivity.

3. Three Terminal BEEM Measurements and Refinement of BEEM Theory

To better test crucial aspects of the existing models of BEEM transport a new three terminal BEEM configuration was developed and successfully used to dynamically vary the electron potential energy barrier at Au - Si interfaces. This was achieved by applying a variable reverse bias voltage to the diode. Varying the reverse bias alters the depth-dependent electron potential barrier width, its sharpness and its peak position in a well defined and reversible way. The BEEM spectra that were obtained as a function of such reverse bias were analyzed using the three-step phase space model of Bell and Kaiser to extract a threshold and scaling factor for each spectrum. From such measurements of the effect of reverse bias on BEEM spectra we were able to demonstrate conclusively that to successfully describe the measurements requires the inclusion of quantum mechanical reflection and image forces on the transport, as well as the existence of significant electron scattering in the semiconductor region.

4. Ion Beam Effects on Ballistic Transport in Processed Metal-Semiconductor Interfaces

A major effort in this project was the examination and successful analysis of the effects of the controlled introduction of defects by selected area ion implantation of Ga+ and Au^+ ions into Au/GaAs interfaces. Using a scanned Focused Ion Beam (FIB), ion energies from 10 keV to 30 keV were used to introduce damage at different depths and degrees. Locally implanted diodes were subsequently characterized using BEEM. We were able to do this such that the same sample had a variety of narrow implanted regions within one BEEM imaging area. Perhaps not surprising is the result that damage confined to the Au layers did not have an pronounced effect on the BEEM spectrum. Damage near the interface drastically reduced the electron transmission with little change in the barrier height. We characterized this reduction in BEEM current as a function of implant dose, in comparison to the transmission of the adjacent undamaged control region. We concluded that one of the primary mechanisms for the irreversible changes in the BEEM spectra is the creation of vacancies in the metal near the semiconductor surface that are subsequently occupied by Ga diffusing from the GaAs. There is also the creation of point defects in the semiconductor. The magnitude of both of these processes was

estimated as a function of implant dose. This work led directly to the development of a more detailed model of BEEM spectra.

Previous models of BEEM, which originated with the JPL group, have two fitting parameters: a threshold energy equivalent to the Schottky barrier height, and an energy-independent scaling factor R. The scaling factor solely accounts for scattering losses, as explicit expressions for loss mechanisms are not in these models. The purpose of our work was to quantify the scattering mechanisms in electron transport in both undamaged and damaged systems. Four mechanisms were modeled in our analysis of the data: quantum mechanical transmission at the interface, optical phonon scattering in the semiconductor, scattering from implantation induced defects in the semiconductor and finally implantation and non-implantation induced scattering in the metal layer. These were successively added to the latest version of BEEM transport model that had been presented previously by Ludeke and Bauer. If we do not allow a transmission factor R as a free parameter in either case, our more refined model, which explicitly included more scattering phenomena, gave a substantially better prediction of the measured current than did the more simple model of Ludeke and Bauer. With our model the un-implanted data were fit particularly well. However, fits to the spectra vs. implant dose did not fit as well, although the fit is better than provided by the Ludeke and Bauer model. This indicated that the amount or effect of the implantation induced defects were still not properly estimated. Since in other work we saw strong indications of unexpected inelastic scattering from atomic vacancies created by hot electron injection, this observation lends support to the possibility that in general the ballistic electron scattering effects of point defects, once they are of sufficient density to be observable, are not yet well understood.

5. Hot Electron Modification Experiments

In order to better quantify and understand the hot electron modification effects that we had previously induced and studied in Au - Si Schottky barrier systems, we pursued a series of experiments involving STM ballistic electron stressing of different variations of the Au - Si system. Si surfaces were prepared with monolayer Pt passivation layers, and then subsequently covered by an inert C layer or some other nonreactive monolayer. This was followed by a thin Au overlayer, which formed the Schottky diode. The inert layer was sufficiently thin that a readily measured BEEM I- V characteristic could be obtained with these

structures. If electrons were then injected into this system with energy of the order of 3 eV or greater, Au adatom/vacancy pairs were generated at the Au - C interface. If a sufficient dose of electrons was applied the result would be the formation of a strong non-equilibrium concentration of vacancies in the region of the Au film immediately under the STM tip. As we had seen earlier in simpler Au - Si diode structures, this strong vacancy concentration in the Au film had the effect of strongly attenuating the BEEM signal. But after time, these vacancies would diffuse to the surface of the Au film or to nearby grain boundaries and annihilate. This would restore the original BEEM image.

When samples were produced without the presence of the Pt passivation layer, and when a strong vacancy concentration was formed in the Au film, there was a permanent quenching of the BEEM signal. This was attributed to the vacancy promoted intermixing of the Au - Si interface, which is generally found to intermix irreversibly on a time scale of approximately 1 day at room temperature in the absence of hot electron injection.

In a different set of experiments STM generated hot electron stressing of Au - GaAs interfaces was found to enhance the BEEM current, but this enhancement annealed away in a few minutes, indicating again that it was associated with some Au atomic diffusion process. In association with a separate study of self assembled monolayers on semiconductors we also observed irreversible BEEM modification of the interface of a gold coated self-assembled monolayer on GaAs. As was the case for the Au - Si system, the threshold for the onset of this irreversible effect is approximately 3 eV indicating that the rate limiting effect is the generation of the Au vacancies which facilitate an intermixing with the underlying GaAs.

A rather interesting observation that has sometimes been obtained with these hot electron stressing experiments has been the "decoration" of grain boundaries in the overlying Au film by the non-equilibrium vacancies. In general, grain boundaries in poly-crystalline metal overlayers are not imaged in BEEM measurements, due to the fairly low probability of an individual electron being strongly scattered by such a boundary. However, as discussed above, high local densities of vacancies can strongly attenuate a ballistic electron beam. As these vacancies diffuse towards a nearby grain boundary and annihilate, we have found that these vacancies can place the grain boundaries in very strong relief when a BEEM image is acquired. Unfortunately, however, this very interesting phenomena is of limited value when one is restricted to room temperature measurements on the Au - Si system, since the rapid vacancy diffusion rate at room temperature is too

rapid for systematic application of this phenomena to the study of point defect diffusion on a nanometer scale. However the potential presented by this observation is most attractive.

IV. PUBLICATIONS AND PH. D. THESES RESULTING FROM CURRENT SUPPORT

Publications

1. **"Ballistic Electron Studies and Modification of the Au/Si Interface,"** A. Fernandez, H. D. Hallen, T. Huang, R. A. Buhrman and J. Silcox, Appl. Phys. Lett. 57, 2826-28 (1990).

2. **"Gold Silicon Interface Modification Studies,"** H. D. Hallen, A. Fernandez, T. Huang, R. A. Buhrman and J. Silcox, Vac. Sci. Technol. B 9, 585-589 (1991).

3. **"Elastic Scattering in Ballistic-Electron-Emission-Microscopy Studies of the Epitaxial $NiSi_2$/Si(111) Interface,"** A. Fernandez, H. D. Hallen, T. Huang, R. A. Buhrman and J. Silcox, Phys. Rev. B. 44, 3428-31 (1991).

4. **"Hot Electron Interactions at the Gold-Silicon Interface,"** H. D. Hallen, A. Fernandez, T. Huang, J. Silcox, and R. A. Buhrman, Phys. Rev. Lett. 69, 2931 (1992).

5. **"Scattering and Spectral Shape in Ballistic Electron Emission Microscopy of $NiSi_2$-Si(111) and Au-Si Samples,"** H. D. Hallen, A. Fernandez, T. Huang, J. Silcox, and R. A. Buhrman, Phys. Rev. B (Rapid Comm.) 46, 7256 (1992).

6. **"Ballistic Electron Emission Microscopy Investigation of SiGe Nanostructures Fabricated Using High Resolution Electron Beam Lithography and Reactive Ion Etching"**, A. Davies, J. G. Couillard, and H. G. Craighead, Appl. Phys. Lett., **61**, 1040 (1992).

7. **"Ballistic Electron Emission Microscopy Investigation of SiGe Nanostructures Fabricated Using Reactive Ion Etching"**, J. G. Couillard, A. Davies, and H. G. Craighead, J. Vac. Sci. Technol. B, **10**, 3112 (1992).

8. **"Ballistic-Electron-Emission-Microscopy Characteristics of Reverse-Biased Schottky Diodes"**, A. Davies and H. G. Craighead, Appl. Phys. Lett., **64**, 2833 (1994).

9. **"Reduced Electron Transmission in Au/GaAs Diodes Damaged by Focused Ion Beam Implantation Studied by Ballistic Electron Emission Microscopy"**, J. W. McNabb, M. Skvarla, and H. G. Craighead, J. Vac. Sci. Technol. B, **12**, 3712 (1994).

Theses

1 **"Ballistic Electron Emission Microscopy Studies of Gold-Silicon Interfaces,"** Hans D. Hallen, Ph.D. Thesis, Cornell University (1991).

2. **"Ballistic Electron Emission Microscopy Studies of the Epitaxial Nickel Disilicide-Silicon Interface System,"** Andres Fernandez, Ph.D. Thesis, Cornell University (1992).

3. **"Ballistic-Electron-Emission Microscopy of Silicon Based Schottky Systems",** A. Davies, Ph.D. Thesis, Cornell University (1994).

4. **"Ballistic Electron Emissions Microscopy Studies of Electron Transport in Au/GaAs Schottky Diodes Damaged by Focused Ion Beam Implantation".** J. W. McNabb, Ph.D. Thesis, Cornell University (1995).

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13. ABSTRACT *(Maximum 200 words)*

This report discusses a completed research program that was generally concerned with the application of Ballistic Electron Emission Microscopy (BEEM) and related scanning tunneling microscopy (STM) techniques to the study of interfacial ballistic transport in a range of electronic materials, and with the extension of BEEM to locally examine aspects and possible applications of electronic scattering processes at both Schottky barrier interfaces and thin film overlayers. The research effort included the demonstration of the high spatial resolution of the BEEM technique, as well as the development of a new model for ballistic electron transport across non-epitaxial Schottky barrier interfaces. The research effort also included the development of a new three terminal BEEM measurement configuration that successfully tested and extended important aspects of the theoretical understanding of BEEM. The effects of ion beam etching and implantation on ballistic transport in processed metal-semiconductor interfaces were also examined, and from these experiments a more complete model of BEEM transport was established. Finally hot electron modification and subsurface ballistic electron lithography effects in various types of Au - Si Schottky barrier systems were extensively studied and a successful microscopic description of this phenomena established.

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